INFRARED AND RAMAN SPECTRA OF 1,1-DIMETHYLHYDRAZINE AND TRIMETHYLHYDRAZINE

[1]This research was carried out under Contract N6 ONR-269, Task Orders III, V, and X of Office of Naval Research

by E. R. Shull[2], J. L. Wood[3], J. G. Aston and D. H. Rank

[2]Present Address: Tonawanda Laboratory, Linde Air Products Company Division of Union Carbide and Carbon Corp., Tonawanda, New York

[3]Present Address: Department of Chemistry and Biology, Sir John Cass College Aldgate, England

Infrared spectra of 1,1-dimethylhydrazine between 700 and 1600cm^{-1} for the gas phase and between 700 and 3500cm^{-1} for the liquid phase and of trimethylhydrazine between 700 and 3500 cm^{-1} for the gas and liquid phases are reported along with the Raman spectra of the two compounds. Frequency assignments are given for both compounds.

I INTRODUCTION

The fundamental frequencies of 1,1-dimethylhydrazine and trimethylhydrazine were needed for calculations of the entropy of their vapors followed by comparison with the calorimetric values to yield values of the barriers hindering internal rotation about the N-N bond in the two compounds. Such a comparison has already been made for hydrazine[4], methylhydrazine[5] and 1,2-dimethylhydrazine[6].

---

[4]D. W. Scott, J. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Am. Chem. Soc., 71, 2293 (1949).

[5]J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, J. Am. Chem. Soc., 73, 1939 (1951).

[6]J. G. Aston, J. G. Janz and K. E. Russell, J. Am. Chem. Soc., 73, 1943 (1951).

II EXPERIMENTAL

(a) Materials. - In both cases part of the calorimetric samples were used. The 1,1-dimethylhydrazine had 0.01 mole per cent impurity[7], and the trimethylhydrazine had

[7] J. G. Aston, J. L. Wood and T. P. Zolki, J. Am. Chem. Soc., 76, 0000 (1954).

2.1 mole per cent impurity[8]. The high percentage impurity in the latter case was due

[8] J. G. Aston and T. P. Zolki. To be published.

to the difficulty of preparation and a very closely boiling impurity which was difficult to remove by fractional melting with the quantity of sample at our disposal.

(b) Raman Spectra. - The Raman spectra were obtained with a three-prism spectrograph[9].

[9] D. H. Rank, R. Scott, and M. R. Fenske, Ind. Eng. Chem., Anal. Ed. 14, 816 (1942).

Excitation was the mercury blue line, 4358A, produced by a pair of low pressure mercury arcs[10] using a filter consisting of saturated aqueous sodium nitrite solution in two

[10] D. H. Rank and J. S. McCartney, J. Opt. Soc. Am. 38, 279 (1948); D. H. Rank, N. Sheppard, and G. J. Szasz, J. Chem. Phys. 16, 698 (1948).

cylindrical condensers. Eastman 103a-O spectroscopic plates backed with opaque red were used. The Raman shifts were determined from measurements on comparison spectra made using an iron-chromium (stainless steel) arc with a 20" f/8 camera (giving a linear dispersion of 19A/mm. at 4600A.) for the 1,1-dimethylhydrazine and with a 10" f/3.5 camera[11] (dispersion 32A/mm. at 4600A) for the trimethylhydrazine. Qualitative

[11] D. H. Rank, J. Opt. Soc. Am. 40, 462 (1950).

depolarization determinations were obtained photographically by the method of polarized incident light[12] using a 5" f/2 camera[11]. Exposure time up to 40 hr. were used.

[12] A. E. Douglas and D. H. Rank, J. Opt. Soc. Am. 38, 281 (1948); D. H. Rank, B. D. Saksena, and E. R. Shull, Disc. Faraday Soc. No. 9, 187 (1950).

(c) Infrared Spectra. - The infrared spectra of the liquid and gas phases of the two compounds were obtained with a Perkin-Elmer Model 120 infrared spectrometer which had been modified to the Walsh double-pass optical arrangement[13] and equipped with

[13] A. Walsh, J. Opt. Soc. Am. 42, 96 (1952).

prisms of lithium fluoride, sodium chloride, and potassium bromide. The gas phase spectra were obtained with a 10 cm. cell at two pressures, a lower pressure to obtain detail in the strong bands and a higher one to detect weaker bands. The data on the two compounds are recorded in Tables I and II.

III DISCUSSION

In considering the spectrum of 1,1-dimethylhydrazine comparison was made with the assignment for trimethylamine[14] when assigning frequencies to the skeletal modes. This is

[14] J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen and H. F. Zuhr, J. Am. Chem. Soc., 66, 1171 (1944).

justified by the fact that the present molecule has an approximate geometrical symmetry of C_{3v} and the N-N force constant is not greatly different to that of C-C as can be seen by comparing the spectrum of methyl hydrazine[15] with that of dimethyl amine.

[15] D. W. E. Axford, G. J. Janz, and K. E. Russell, J. Chem. Phys. 19, 704 (1951).

Regard was paid to this approximate symmetry in making use of the polarizations as a guide in the assignments. In assigning the NH stretching and bending frequencies comparison was made with the spectrum of methylhydrazine[15].

In assigning frequencies to the skeletal modes of trimethylhydrazine comparison was made with iso-pentane[16] and when treating the NH stretching and bending comparison

---

[16]S. C. Schumann, J. G. Aston and Malcolm Sagenkahn, J. Am. Chem. Soc. 64, 1039 (1942)

---

was made with sym. dimethylhydrazine[15].

The assignment is given in Table III while Table IV gives the explanation of frequencies unassigned for 1,1-dimethylhydrazine as combinations of assigned frequencies. In the case of trimethylhydrazine there are six unassigned combination bands between 2458 and 2685cm^{-1} in the liquid infrared which do not appear in the liquid Raman spectrum. No attempt is made to assign these bands.

TABLE I

INFRARED AND RAMAN SPECTRA 1,1-DIMETHYLHYDRAZINE

Infrared (Gas)			Infrared (Liquid)			Raman (Liquid)			
ν	I[a]	Structure	ν	I[a]	Structure	$\Delta\nu$	I[a]	Pol.[b]	Breadth
						282	(w)	(p)	Diffuse & broad
						418	(m)	(p)	Narrow
						445	(m)	(p)	Narrow with diffuse wing at longer λ
803	(vs)	pqr	793	s	Broad	809	vs	p	Narrow
904	(s)	pqr	848	?					
961	m	q	944	s	Broad	957	w	pp?	Diffuse
1016	vw		1009	s	Broad	1027	m	p	Narrow
1046	vs	pqr							
1090	m	q	1069	s	Broad	1061	w	pp	Diffuse but not too broad
1139	s	q?	1140	s	?	1150	s	p	Narrow
1153	Branch on 1139								
1214	m	pqr	1201	s	?	1212	m	dp?	Narrow
			1243	m	?	1248	m	pp	Diffuse but narrow
1301	m	pqr	1321	s	?	1325	vvw	dp?	Diffuse
						1405	m	dp	Narrow
1457	m	pqr		vs		1423	s	dp	Broad
1593	m	?	---			1599	w	pp	Diffuse
			2764	m		2774	?		Covered by Hg line
			2811	m-		2817	?	p?	Narrow blends into Hg line
			2844			2849	m-s	p	Narrow
						2881	w	p	Narrow
			2944	m		2950	s	p	Narrow
			2975	w		2988	m	dp	Diffuse
			3126	vw		3141	m	p	Narrow
			3298	w		3330	vw	dp?	Diffuse

[a] vvw, vw, m, s, vs denote respectively: extremely weak, very weak, weak, medium, strong and very strong.

[b] dp, pp, sp denote respectively: depolarized, partly polarized, and polarized.

TABLE II

INFRARED AND RAMAN SPECTRA OF TRIMETHYLHYDRAZINE

Infrared (Gas)			Infrared (Liquid)			Raman (Liquid)			
ν	I[a]	Structure	ν	I[a]	Structure	ν	I[a]	Pol.[a]	Breadth
						307	(w)	dp	Diffuse
						414	m	dp	Narrow
						436	m	p	Narrow
						498	s	p	Narrow
712	vw		688	vw					
783	vs		739	vs	Broad	747	s	pp	Narrow
888	vs		883	vs	Broad	884	m	p	Diffuse
1007	vs	Broad	958	m	Sharp	965	m	dp	Narrow
1044	w		1005	m	Sharp	1013	m	dp?	Narrow
			1077	m	Sharp	1083	m	pp	Narrow
1134	s		1119	m	Sharp	1126	ms	p	Narrow
1168	m		1165	w					
1180?	m		1189	m	Sharp				
1270	m		1212	m	Sharp	1215	w	dp	Diffuse
						1398	m	dp	Narrow
1477	s		1485	s	Broad	1448	s	dp	Broad and diffuse
			2458						
			2485						
			2535						
			2571						
			2593						
			2685						
2858	s		2858	vs		2843	m?	dp?	
2970	s		2970	vs		2987	vs	dp	Broad
3082	m					3032	s	dp?	Narrow
3092	m	Sharp	3194	m					
3405	m		3405	vw		ca. 3400	m	p	Narrow

[a] See notes at foot of Table I

Table III

ASSIGNMENTS FOR 1,1-DIMETHYLHYDRAZINE - TRIMETHYLHYDRAZINE

1,1-Dimethylhydrazine		Trimethylhydrazine	
Assignment	**Frequency**	**Assignment**	**Frequency**
Skeletal bend	418	Skeletal bend	307
" "	445 (2)	" "	414
Skeletal stretch	803	" "	436
" "	904	" "	498
" "	961	Skeletal stretch	712
Rocking	961	" "	783
"	1046 (2)	" "	888
"	1090 (2)	" "	1007
"	1139	CH_3 rock	1044 (2)
CH_3 bend	1301 (4)	" "	1134 (2)
" "	1405	" "	1168 (2)
" "	1457	NH bend	1180
NH_2 bend	1593	" "	1270
CH_3 stretch	2950 (3)	CH_3 bend	1398 (3)
" "	2988 (3)	" "	1477 (6)
NH_2 "	3741	CH_3 stretch	2858 (4)
" "	3330	" "	2970 (2)
		" "	3082
		" "	3092 (2)
		NH stretch	3405

Table IV

COMBINATION FREQUENCIES FOR 1,1-DIMETHYLHYDRAZINE

Infrared (gas)	Raman (Liquid)	Combination
1214	1212	418 + 803
	2774	418 + 803 + 1593
	2817	1405 + 1423
	2849	2 x 1457
	2881	1593 + 1301